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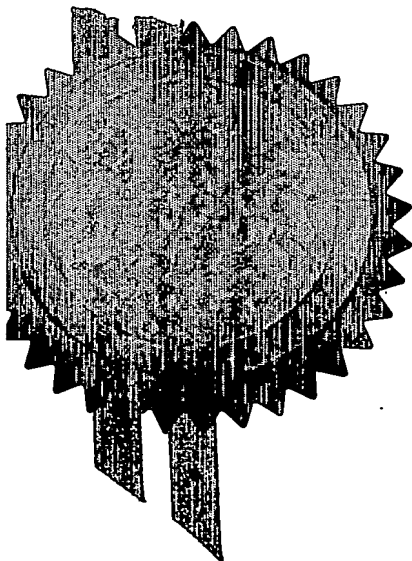
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Patent application number

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Full name, address and postcode of the or of
each applicant (underline all surnames)Avecia Limited
Hexagon House
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Manchester, M9 8ZS

Patents ADP number (if you know it)

07764137001 ✓

If the applicant is a corporate body, give the
country/state of its incorporation

GB

Title of the invention

COMPOUND

Name of your agent (if you have one)

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Patents ADP number (if you know it)

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Abstract

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I/We request the grant of a patent on the basis of this application.

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G. Terry

Date 28/8/02

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Mrs K.M. Pinder/Miss G. Terry 0161 721 1361/2

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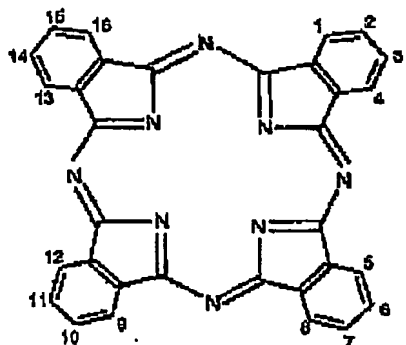
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COMPOUND

This specification describes an invention relating to certain poly(substituted)-phthalocyanine compounds which absorb in the near infra-red region of the electromagnetic spectrum, e.g. from 750 to 1500 nm, and more especially from 750 to 1100 nm, to the use of the compounds in a variety of applications where it is desirable to absorb infra-red radiation including systems and compositions providing protection against the effects of such radiation or requiring localised heat input and to systems and compositions incorporating the compounds.

EP 0155780 describes various generic classes of infra-red absorbing phthalocyanine compounds in which (a) each of at least five of the peripheral carbon atoms in the 1, 4, 5, 8, 9, 12, 13 & 16 positions of the phthalocyanine nucleus shown in Formula A

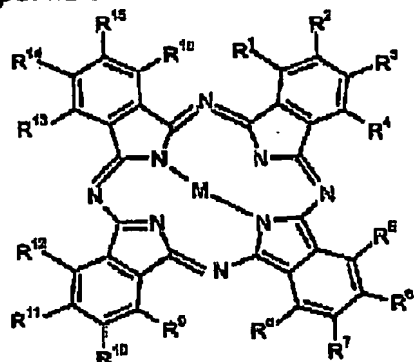


Formula A

(these eight positions being hereinafter referred to as the "3,6-" positions by analogy with the equivalent 3- and 6-positions in the four molecules of phthalonitrile from which the phthalocyanine is derivable) is linked by an atom from Group VB or Group VIB of the periodic Table (other than oxygen) to a carbon atom of an organic radical and (b) the phthalocyanine nucleus is metal free or is complexed with a metal or oxy-metal. The only specific disclosure of such a compound carrying an oxy-metal is octa-3,6-(4-t-butylphenylthio)-VOPc (in which VOPc represents a phthalocyanine nucleus complexed with the oxymetal group VO and each of the eight peripheral carbon atoms in the "3,6-" positions on the phthalocyanine carries a 4-t-butylphenylthio group). Apart from being an infra-red absorber, no other properties are disclosed for this specific compound.

Although the compounds disclosed in EP 0155780 have a strong absorption peak in the near infra-red region of the electromagnetic spectrum and some have been commercialised, they generally exhibit some absorption in the visible region of the spectrum (because the position of the infra-red absorption peak is close to the visible region) and thus have a faint coloration, when applied to a substrate, which is detectable to the eye unless masked with another coloured species.

According to a first aspect of the present invention there is provided a phthalocyanine compound of Formula I



Formula I

wherein at least 5 of the groups represented by R^1 , R^4 , R^5 , R^6 , R^9 , R^{12} , R^{13} & R^{16} are independently $-X-J$ or $-X-L-X^1$, wherein

each J is independently selected from C_{1-8} -alkyl; C_{2-8} -alkenyl; C_{4-8} -cycloalkyl (each being optionally substituted by a group selected from C_{1-4} -alkoxy, C_{1-4} -alkylthio, C_{6-12} -aryl, C_{6-12} -arylthio, C_{1-4} -alkylsulphonyl, C_{1-4} -alkylsulphonylamino, C_{1-4} -alkylsulphoxide, amino, mono- and di- C_{1-4} -alkylamino, halogen, nitro, cyano and hydroxycarbonyl ($-COOH$), hydroxysulphonyl ($-SO_3H$) or dihydroxyphosphonyl ($-PO_3H_2$) or C_{1-4} -alkyl esters thereof) and from C_{6-12} -aryl (optionally substituted by a group selected from C_{1-3} -alkyl, C_{1-3} -alkoxy, C_{1-3} -alkylthio, C_{1-3} -alkylsulphonyl, C_{1-3} -alkylsulphonylamino, C_{1-4} -alkylsulphoxide, amino, mono- and di- C_{1-3} -alkylamino, halogen, nitro, cyano and hydroxycarbonyl, hydroxysulphonyl or dihydroxyphosphonyl hydroxycarbonyl- C_{1-3} -alkyl, hydroxysulphonyl- C_{1-3} -alkyl, dihydroxyphosphonyl- C_{1-3} -alkyl or C_{1-3} -alkyl esters thereof);

each L is independently selected from C_{1-8} -alkylene and C_{4-8} -cycloalkylene (each being optionally substituted by a group selected from C_{1-4} -alkoxy, C_{1-4} -alkylthio, C_{6-12} -aryl, C_{6-12} -arylthio, C_{1-4} -alkylsulphonyl, C_{1-4} -alkylsulphonylamino, C_{1-4} -alkylsulphoxide, amino, mono- and di- C_{1-4} -alkylamino, halogen, nitro, cyano and hydroxycarbonyl, hydroxysulphonyl or dihydroxyphosphonyl or C_{1-4} -alkyl esters thereof); and from C_{6-12} -arylene (optionally substituted by a group selected from C_{1-3} -alkyl, C_{1-3} -alkoxy, C_{1-3} -alkylthio, C_{1-3} -alkylsulphonyl, C_{1-3} -alkylsulphonylamino, C_{1-3} -alkylsulphoxide, amino, mono- and di- C_{1-3} -alkylamino, halogen, nitro, cyano and hydroxycarbonyl, hydroxysulphonyl, dihydroxyphosphonyl, hydroxycarbonyl- C_{1-3} -alkyl, hydroxysulphonyl- C_{1-3} -alkyl or dihydroxyphosphonyl- C_{1-3} -alkyl or C_{1-3} -alkyl esters thereof);

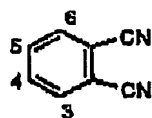
M is an oxymetal group;

each X independently is S, Se, Te or NT;

each X^1 independently is S, Se, Te or NT and directly attached to a peripheral 3,6-carbon atom of another phthalocyanine compound of Formula I;

each T independently is H, alkyl or phenyl, or T & J, together with the N atom to which they are attached, form an aliphatic or aromatic ring provided this N atom is not positively charged; provided where J is aryl, T is not aryl; and the remaining groups from R^1 to R^{16} are independently selected from H, halogen, -OJ, hydroxycarbonyl, hydroxysulphonyl, dihydroxyphosphonyl, hydroxycarbonyl- C_{1-3} -alkyl, hydroxysulphonyl- C_{1-3} -alkyl and dihydroxyphosphonyl- C_{1-3} -alkyl.

Throughout this specification the carbon atoms in the phthalocyanine compound of Formula I to which the groups R^1 , R^4 , R^5 , R^6 , R^9 , R^{12} , R^{13} & R^{16} are attached are referred to as the "3,6-carbon atoms" by analogy with the equivalent 3- and 6-carbon atoms in the four molecules of phthalonitrile (see Formula II) from which this present phthalocyanine compound is derivable. Furthermore the symbols, H_2Pc and MPc , in which M is an oxymetal group, e.g. VO, TiO or MoO, will be used to indicate unmetallised and oxymetallised phthalocyanines, respectively.



Formula II

In the phthalocyanine compound of Formula I, preferably at least six, more preferably at least seven and more especially all eight of the "3,6-carbon atoms" carry a group of the formula -X-J or -X-L- X^1 -. It is further preferred that each "3,6-carbon atom" carries a group of formula -X-J. It is also preferred that the remaining peripheral carbon atoms (hereinafter referred to as the "4,5-carbon atoms") are unsubstituted, i.e. that each of R^2 , R^3 , R^6 , R^7 , R^{10} , R^{11} , R^{14} & R^{15} in Formula I is H.

Compounds of especial interest have an absorption peak from 750 to 1100 nm, more preferably from 800 to 1000 nm, and those of more especial interest have at least 90% (and more especially at least 95%) of their absorption strength at or above 750 nm. Preferred compounds have a narrow half-band width (width of band at half peak height) in solution, especially of less than 60 nm.

Preferred groups represented by J are C_{1-4} -alkyl, such as methyl, ethyl, propyl or butyl, which may be straight or branched chain, but are preferably the former; C_{2-4} -alkenyl, such as vinyl or allyl; cyclohexyl; and more especially phenyl; naphtha-1-yl or naphtha-2-yl, each of which is optionally substituted as hereinbefore defined. Where a substituent on J is electron-withdrawing, such as hydroxycarbonyl, nitro or cyano, it is preferably in the ortho-position with respect to the link between J and X, so that it is not coupled into the extended conjugation system of the Pc nucleus.

Preferred groups represented by L are C_{2-4} -alkylene such as ethylene, prop-1,2-ylene and prop-1,3-ylene; C_6 -cycloalkylene, such as cyclohex-1,4-ylene; phen-1,4-ylene and naphtha-1,4-ylene, each of which is optionally substituted as hereinbefore defined.

Preferred substituents for the aryl and arylene groups represented by J and L are C_{1-2} -alkyl, such as methyl and ethyl; C_{1-2} -alkoxy such as methoxy and ethoxy;

C₁₋₂-alkylthio, such as methylthio and ethylthio; C₁₋₂-alkylsulphonyl; C₁₋₂-alkylsulphoxide; amino; mono- and di-C₁₋₂-alkylamino, such as methylamino and diethylamino; halogen such as chloro or bromo; nitro; cyano; hydroxycarbonyl, hydroxysulphonyl, dihydroxy-phosphonyl, hydroxycarbonyl-C₁₋₃-alkyl, hydroxysulphonyl-C₁₋₃-alkyl and dihydroxy-phosphonyl-C₁₋₃-alkyl and C₁₋₂-alkyl esters thereof, such as -COOH, -COOC₂H₅, -SO₃H, -SO₃CH₃, -PO₃H₂, -CH₂CH₂COOH, -CH₂SO₃H, -CH₂PO₃H₂, -CH₂COOCH₃, and -CH₂CH₂SO₃CH₃. Examples of optionally substituted aryl and arylene groups represented by J and L are phenyl, 4-methylphenyl, 2-methylphenyl, 4-*i*-propylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 3,5-dimethylphenyl, 4-methoxyphenyl, 4-methylthiophenyl, 3-(2-[methoxycarbonyl]ethyl)phenyl, 3-(hydroxycarbonyl)phenyl, 4-(hydroxysulphonyl)-phenyl, 2-chlorophenyl, 4-bromophenyl, 3,5-dichlorophenyl, naphtha-1-yl and naphtha-2-yl.

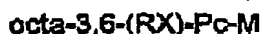
Preferred substituents for the alkyl, alkylene, alkenyl, cycloalkyl and cycloalkylene groups represented by J and L are C₁₋₂-alkoxy or C₁₋₂-alkylthio, such as methoxy, ethoxy and methylthio; C₆₋₁₂-aryl, especially phenyl or naphtha-1-yl; halo or cyano. Examples of optionally substituted alkyl, alkylene, alkenyl, cycloalkyl and cycloalkylene groups represented by J and L are methyl, ethyl, *i*-propyl, methoxy, ethoxy, methylthio, allyl, trifluoromethyl, benzyl, dimethylaminoethyl, methylsulphonylaminoethyl and ethylaminoethyl.

It is preferred that X and X¹ are sulphur (S), selenium (Se) or tellurium (Te) and more especially sulphur. If any group represented by X or X¹ is NT, it is preferred that the compound contains not more than four such NT groups.

Preferred groups represented by T are H; C₁₋₆-alkyl, especially C₁₋₄-alkyl, such as methyl, ethyl or propyl; or phenyl. However, where J or L is aryl, it is preferred that T on the group NT attached thereto, is not aryl. Where T & J, together with the N atom to which they are attached, form an aliphatic or aromatic ring, this is preferably piperidinyl, piperazinyl, morpholinyl or pyrrolinyl.

Examples of suitable oxy-metal groups, represented by M in Formula I are titanyl (TiO), molybdy (MoO) and vanady (VO).

A preferred compound according to the present invention conforms to the following formula:



Formula III

wherein

M is an oxymetal group selected from VO, TiO and MoO;

Pc is the phthalocyanine nucleus;

each X is independently S, Se, Te or NT wherein T is H, C₁₋₄-alkyl or phenyl; and

each R is independently phenyl or naphthyl each of which is optionally substituted by up to 6 groups selected from C₁₋₃-alkyl, C₁₋₃-alkoxy, C₁₋₃-alkylthio, C₁₋₃-alkylsulphonyl, C₁₋₃-alkylsulphonyl-amino, C₁₋₃-alkylsulphoxide, amino, mono- and di-C₁₋₃-alkylamino, halogen, nitro, cyano and hydroxycarbonyl, hydroxy-sulphonyl,

dihydroxyphosphonyl, hydroxycarbonyl-C₁₋₃-alkyl, hydroxysulphonyl-C₁₋₃-alkyl or hydroxyphosphonyl-C₁₋₃-alkyl or C₁₋₃-alkyl esters thereof; or

R & T together form a piperidinyl, piperazinyl, morpholinyl or pyrrolinyl ring.

Examples of compounds of the present invention conforming to Formula I and

5 Formula III are:

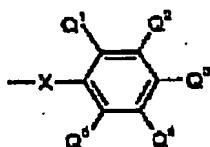
octa-3,6-(phenylthio)-TiOPc
octa-3,6-(4-methylphenylthio)-VOPc
octa-3,6-(2-methylphenylthio)-VOPc
octa-3,6-(2-ethylphenylthio)-VOPc
10 octa-3,6-(4-i-propylphenylthio)-TiOPc
octa-3,6-(2-i-propylphenylthio)-VOPc
octa-3,6-(2,4-dimethylphenylthio)-VOPc
octa-3,6-(2,5-dimethylphenylthio)-VOPc
octa-3,6-(3,5-dimethylphenylthio)-VOPc
15 octa-3,6-(4-methoxyphenylthio)-VOPc
octa-3,6-(4-n-propoxyphenylthio)-MoOPc
octa-3,6-(4-methylthiophenylthio)-TiOPc
octa-3,6-(4-methylthiophenylthio)-VOPc
octa-3,6-(3,4-dimethylphenylthio)-VOPc
20 octa-3,6-(3-methoxycarbonylphenylthio)-MoOPc
octa-3,6-(3-hydroxycarbonylphenylthio)-VOPc
octa-3,6-(2-[hydroxycarbonylmethyl]phenylthio)-VOPc
octa-3,6-(3-[2-hydroxycarbonyl-ethyl]phenylthio)-VOPc
octa-3,6-(4-[3-hydroxycarbonyl-n-propyl]phenylthio)-VOPc
25 octa-3,6-(4-hydroxysulphonylphenylthio)-VOPc
octa-3,6-(4-hydroxyphenylthio)-VOPc
octa-3,6-(naphtha-1-ylthio)-VOPc
octa-3,6-(naphtha-2-ylthio)-VOPc
octa-3,6-(2-chlorophenylthio)-VOPc
30 octa-3,6-(4-bromophenylthio)-TiOPc
octa-3,6-(3,5-dichlorophenylthio)-MoOPc
octa-3,6-(benzylthio)-VOPc
octa-3,6-(phenyltelluro)-VOPc

and octa-3,6-(butylthio)-MoOPc.

35 Examples of compounds of the present invention conforming to Formula I are:

hepta-3,6-(2,4-dimethylphenylthio)-mono-3,6-chloro-VOPc
hepta-3,6-(4-bromophenylthio)-mono-3,6-chloro-TiOPc
hexa-3,6-(4-methylphenylthio)-di-3,6-chloro-VOPc
hexa-3,6-(2,5-dimethylphenylthio)-di-3,6-chloro-MoOPc
40 and penta-3,6-(2-methoxyphenylthio)-tri-3,6-chloro-TiOPc.

Although the groups attached to the eight "3,6-carbon atoms" may be different, they are preferably identical and each is more preferably an optionally-substituted phenyl group of the Formula IV:



Formula IV

wherein each of Q¹ to Q⁵ is independently selected from H, C₁₋₃-alkyl, more especially methyl; C₁₋₃-alkoxy more especially methoxy; C₁₋₃-alkylthio, more especially methylthio; C₁₋₃-alkylsulphonyl, C₁₋₃-alkylsulphonylamino, C₁₋₃-alkylsulphoxide, amino, mono- and di-C₁₋₃-alkylamino, halogen, nitro, cyano and hydroxycarbonyl, hydroxysulphonyl, dihydroxyphosphonyl, hydroxycarbonyl-C₁₋₃-alkyl, hydroxysulphonyl-C₁₋₃-alkyl or hydroxyphosphonyl-C₁₋₃-alkyl or C₁₋₃-alkyl esters thereof. In the phenyl group of Formula IV, Q² and Q⁴ are both preferably H. It is further preferred that Q¹, Q³ and Q⁵ are not electron-withdrawing groups, such as hydroxycarbonyl, nitro or cyano.

The present compounds in which the groups represented by J and/or L contain a hydroxycarbonyl, hydroxysulphonyl or hydroxyphosphonyl group (especially in the salt form), generally have increased hydrophilicity (and solubility in aqueous media) and reduced hydrophobicity (and solubility in organic media) compared with compounds which do not contain such a group. Hydrophilicity (and aqueous solubility) also may be effected and/or enhanced by sulphonation and/or phosphorylation of the present compounds whereby hydroxysulphonyl and/or dihydroxyphosphonyl groups may be introduced onto carbon atoms in the phthalocyanine nucleus itself or in the pendant phenyl or naphthyl groups attached thereto. This facility for enhancing hydrophilicity by sulphonation and/or phosphorylation is an important feature of the present compounds because it has been found that the introduction of such groups has a minimal effect on their other properties, especially the position of their absorption peak in the IR region of the spectrum. Thus a solvent soluble compound according to the present invention may be rendered more hydrophilic (and thus its aqueous solubility increased) merely by sulphonation without affecting its infra-red absorbing properties.

The present compounds may be prepared by the processes described in EP 0155780 A for the preparation of the analogous first preferred class of compounds described therein.

Compounds according to the present invention (and more especially those of Formula III) have a narrow main absorption peak (half-band width generally less than 60 nm) in the infra-red region of the electromagnetic spectrum and this peak is bathochromically displaced with respect to the compounds disclosed in EP 0155780 so that they have a fainter coloration and are thus less easily detectable by visual inspection when applied to a substrate. The present compounds are also generally more thermally

stable and resistant to fading under the effects of illumination by electromagnetic irradiation than octa-3,6-(4-t-butylphenylthio)-VOPc.

The present compounds are particularly useful as infra-red absorbers (IRA) in the following applications:

- (a) Heat Input Systems, wherein it is desired to input heat at specific locations by exposure to infra-red radiation, e.g. in electrophotography where laser-induced fixation of the latent toner image is enhanced by the presence of the IRA in the toner, in print plate manufacture where the presence of the IRA in the photosensitive layer on a lithographic print plate enhances the formation of the laser-induced image on the print plate, and in polymer welding wherein laser-induced heat generation in the vicinity of the weld is enhanced by the presence of the IRA;
- (b) IR Radiation Protection Systems, wherein it is desired to absorb infra-red radiation from incident radiation in order to protect a subject from the effects of this radiation, e.g. in heat resistant ("solar") glazing for buildings or cars, in sun visors and in welding goggles; and
- (c) Detection/Handling Systems wherein it is desired to provide or enhance a machine-detectable IR or heat energy signal for use in medical treatment, e.g. in tracing the movement of a drug doped with the IRA, enhancing a thermal signal in thermal imaging, fault detection, e.g. detecting cracks flooded with a solution of the IRA, and automated detection and/or manipulation of articles marked with the IRA, e.g. in mail sorting or in machine reading of prices and related information in supermarket operations.

According to a second aspect of the present invention there is provided a method for the production of a lithographic printing plate containing a photosensitive layer comprising irradiating the photosensitive layer with an infra-red laser in accordance with pattern information wherein the photosensitive layer comprises an IRA according to the first aspect of the present invention.

According to a third aspect of the present invention there is provided a method of polymer welding in which a polymer material is irradiated with an infra-red laser in a region where it is desired to form a weld wherein the polymer material comprises an IRA according to the first aspect of the present invention.

According to a fourth aspect of the present invention there is provided a method for the protection of the interior of a glazed structure against the heating effect of incident IR radiation by incorporating into the glazing or a layer forming part of the glazing an IRA according to the first aspect of the present invention.

According to a fifth aspect of the present invention there is provided a method for the attenuation of IR irradiation passing through a protective transparent film (such as a visor or eyepiece of goggles) by incorporating into the protective film or a layer forming part of the protective film an IRA according to the first aspect of the present invention.

According to a sixth aspect of the present invention there is provided a method for detecting an article carrying a superficial image by scanning with an infra-red detector wherein the image comprises an IRA according to the first aspect of the present invention.

5 According to a seventh aspect of the present invention there is provided a method for the formation of a permanent toner image on a substrate using an electrophotographic device incorporating an IR source, in order to fix the temporary toner image on the substrate and/or provide an IR-readable permanent toner image, wherein the toner comprises an IRA according to the first aspect of the present invention.

10 According to an eighth aspect of the present invention there is provided a method for enhancing a thermal signal from a process by incorporating into the process medium an IRA according to the first aspect of the present invention.

15 According to a ninth aspect of the present invention there is provided a method for the detection of passages through an IR permeable solid by applying to the solid a liquid containing an IRA according to the first aspect of the present invention to the solid and examining the solid for the presence of the IRA therein.

20 According to a tenth aspect of the present invention there is provided an article carrying an image adapted for machine reading in response to a reflective signal generated by scanning the image with infra-red radiation wherein the image comprises an IRA according to the first aspect of the present invention, especially for use in the automated recognition and handling and/or sorting of articles, such as mail and super-markets goods.

In the aforementioned applications where the IRA is applied to a surface, this may be effected by dissolving or dispersing it into a liquid medium so as to form an ink and applying the ink to the surface using an appropriate printing technique.

25 According to an eleventh aspect of the present invention there is provided an ink comprising an IRA according to the first aspect of the present invention in an ink medium.

30 A first preferred ink according to the eleventh aspect of the present invention also comprises a colorant. Such an ink in which the colorant and IRA are both dissolved in the ink medium is generally suitable for use in the ink jet printing of absorbent materials such as paper and card.

A second preferred ink according to the eleventh aspect of the present invention also comprises an alkoxyated or polyalkoxyated acrylate monomer, a photoinitiator and a colorant (as hereinafter further described).

35 (a) Heat Input Systems

(i) Conventional Toner

A suitable flash fixing toner comprises a binder resin, a coloring agent and an IRA according to the present invention, in which the IRA is preferably present in an amount from about 0.01% to 1.0% (more preferably around 0.1%) by weight, based on the total

amount of the toner. The IRA is conveniently dispersed (or dissolved) in the binder resin forming the matrix of the toner particles.

The binder resin may be any suitable resin used in flash fixing toners, such as polystyrenes; co-polymers of styrene with (meth)acrylic esters, acrylonitrile, or maleic esters; poly(meth)acrylic esters; polyesters; polyamides; epoxy resins; phenolic resins; hydrocarbon resins; and petroleum resins, which may be used alone or in combination with each other or with other resins or additives. Preferred resins are polyester resins and epoxy resins of Bisphenol A and epichlorohydrin.

The colorant may be any of those suitable for use in flash fixing toners, for example one or more pigments or dyes, such as, chrome yellow, cadmium yellow, yellow iron oxide, titan yellow, naphthol yellow, Hanza yellow, pigment yellow, benzidine yellow, permanent yellow, quinoline yellow, anthrapyrimidine yellow, permanent orange, molybdenum orange, vulcan fast orange, benzidine orange, indanthrene brilliant orange, iron oxide, amber, permanent brown, rose iron oxide red, antimony powder, permanent red, fire red, brilliant carmine, light fast red toner, permanent carmine, pyrazolone red, Bordeaux, helio-Bordeaux, rhodamine lake, DuPont oil red, thioindigo red, thioindigo maron, watching red strontium, cobalt purple, fast violet, dioxane violet, methyl violet lake, methylene blue, aniline blue, cobalt blue, cerulean blue, chalco oil blue, nonmetal phthalocyanine blue, phthalocyanine blue, ultramarine blue, indanthrene blue, indigo, chrome green, cobalt green, pigment green B, green gold, phthalocyanine green, malachite green oxalate and polychromo-bromo copper phthalocyanine. The amount of colorant agent may be varied widely but is preferably present in an amount from 3 to 15 parts by weight, based on 100 parts by weight of the binder resin.

The flash fixing toner may incorporate further components, such as a wax, a charge control agent and/or a flow-enhancer.

The wax may be a polyolefin type or natural wax, such as carnauba wax, montan wax, and a natural paraffin, polyethylene, polypropylene, polybutylene, ethylene-propylene copolymer, ethylene-butene copolymer, ethylene-pentene copolymer, ethylene-3-methyl-1-butene copolymer, and copolymers of olefins with other monomers, such as vinyl esters, halo-olefins, (meth)acrylic esters, and (meth) acrylic acid or derivatives. The weight-average molecular weight of the waxy component is preferably from 1,000 to 45,000 daltons.

Examples of suitable charge control agents are nigrosine, monoazo dyes, zinc, hexadecyl succinate, alkyl esters or alkyl amides of naphthoic acid, nitrohumic acid, N,N-tetramethyl diamine benzophenone, N,N-tetramethyl benzidine, triazines and metal complexes of salicylic acid. If the colorant is other than black, it is preferred that the charge control agent is substantially colourless.

Example of suitable flow-enhancing agents are minute particles of inorganic substances, such as colloidal silica, hydrophobic silica, hydrophobic titania, hydrophobic

zirconia, and talc and minute particles of organic substances, such as polystyrene beads and (meth)acrylic resin beads.

If the IRA is soluble or dispersible in the relevant binder resin, the coloring agent and IRA (and any other components mentioned above) are preferably compounded and kneaded together. After cooling and pulverizing the resultant mixture, the particles are classified.

(ii) Chemically Produced Toner

An IRA according to the present invention may be incorporated into a chemically produced toner. The toner may comprise one or more polymers, mixtures of polymers being appropriate where polymers of different molecular weight are used to control the molecular weight distribution and the melt rheology properties of the toner. Examples of suitable polymers are styrene-acrylate copolymers, styrene-butadiene copolymers, polyesters and hydrocarbon resins. The toner may incorporate colorant to provide a coloured image on the printed substrate, charge control agent to enhance uptake of electrical charge and wax to aid release from the fusion roller. Suitable colorants are pigments (including magnetic pigments, provided these do not interfere with the absorption of infra-red radiation by the IRA) and dyes. Suitable charge control agents include metal complexes, such as complexes of Zn, Al, Fe or Cr, and polymeric materials, such as phenolic polymers. Suitable waxes include hydrocarbon waxes, such as paraffin, polyethylene or polypropylene waxes, waxes derived from carbon monoxide and hydrogen, such as Fischer-Tropsch waxes, natural product waxes, such as carnauba wax, and synthetic waxes, such as ester or amide waxes. The toner may also contain surface additives, such as silica, titania, alumina or polymeric particles, to control flow, charging performance or transfer properties.

(iii) Offset Printing Plate Production

Offset printing plates are generally prepared from a recording material comprising a substrate and a photosensitive image layer formed on the front of said substrate, permitting a desired pattern to be formed on the image layer by irradiation with a suitable source of electromagnetic radiation. One known recording material contains an IRA incorporated in the image layer and the desired pattern is formed by irradiation with IR radiation, generally from a laser, in accordance with prescribed pattern information. The present IRA is suitable for use in such a recording material especially for use in conjunction with an IR laser with an emission peak in the region of 760 nm to 1000 nm, such as the commercially available solid-state laser diode with a main emission peak at about 830 nm. Recording materials for offset printing plates in which the present IRA can be incorporated into the photosensitive layer are described in US 6,294,298 and the publications disclosed therein.

(iv) Laser Welding

An example of laser welding is given in GB-A-2,276,584 which provides a method for welding together two bodies of thermoplastic material (one of which is substantially transparent to infra-red radiation and the other substantially opaque) held with two adjacent surfaces in contact (defining a contact region between the two bodies) by irradiating the surface of the opaque body in the contact region with infra-red radiation through the transparent body whereby the surfaces of both bodies in the contact region may be heated to a temperature at which they fuse and become joined together by a fusion weld, through absorption of ir radiation by the opaque body in the contact region and transmission of heat thereby generated to the ir-transparent body in the contact region. The opacity of the opaque thermoplastic body may be enhanced by the addition of an IRA according to the first aspect of the present invention

Using this method, thermoplastic pipe can be radially reinforced by winding one or more layers of fibre reinforced thermoplastic tape or film around the pipe. The tapes are conveniently wound on the pipe in pairs, in which the tapes are of opposite hand to balance the torsional forces when the pipe is conveying a product under pressure. Each tape is wound under tension which serves to hold the tape and pipe in close contact in order to ensure that a fusion weld is formed between them during the subsequent welding stage. The first tape in the pair is applied directly to the pipe and the second tape applied on top of the first tape under sufficient tension to hold both tapes firmly against the pipe so that they become fused thereto in the welding stage. Further tapes, singly or in pairs, can be wound on top of the first pairs to provide additional reinforcement. Typically each tape is composed of polyethylene and contains a number of reinforcing fibres extending lengthwise of the tape and evenly distributed across its width. Each fibre is conveniently composed of a bundle of fine filaments of a suitable reinforcing material, such as aramid. Alternatively, a pipe may be longitudinally reinforced by applying the reinforcing tape along the length of the pipe so that the strength of the tape is parallel to the longitudinal axis of the pipe. In both these examples, the tape constitutes the substantially IR-transparent body, the pipe constitutes the IR-opaque body and the fusion weld is formed by irradiating the pipe with IR radiation from the outside, through the reinforcing tapes, in order to effect fusion of the layers of thermoplastic material adjacent to the contact layer between the inner surfaces of the tapes and the outer surface of the pipe.

(b) IR Radiation Protection Systems

(i) Heat Resistant Glazing

An IRA according to the present invention may be used as the wavelength gap-filling component (WGFC) of an optical body of the type described in US 6,049,419 (the contents of which are incorporated herein) comprising either:

- 1 (a) a birefringent dielectric multilayer film, which may be a polarizer, mirror, or both, having a reflecting band positioned to reflect infrared radiation of at least one

polarization at an incident angle normal to the film, said reflecting band having a short wavelength bandedge $\lambda_s 0$ and long wavelength bandedge $\lambda_l 0$ at a normal incident angle, and a short wavelength bandedge $\lambda_s \theta$ and long wavelength bandedge $\lambda_l \theta$ at a maximum usage angle θ , wherein $\lambda_s \theta$ is less than $\lambda_s 0$ and $\lambda_l 0$ is selectively positioned at a wavelength greater than about 700 nm; and

(b) a component which at least partially absorbs or reflects radiation in the wavelength region between $\lambda_s \theta$ and $\lambda_l 0$ at a normal angle of incidence (WGFC); or

2. (a) an isotropic dielectric multilayer film having a reflecting band positioned to reflect infrared radiation of at least one polarization at an incident angle normal to the film, said reflecting band having a short wavelength bandedge $\lambda_s 0$ and long wavelength bandedge $\lambda_l 0$ at a normal incident angle, and a short wavelength bandedge $\lambda_s \theta$ and long wavelength bandedge $\lambda_l \theta$ at a maximum usage angle θ , wherein $\lambda_s \theta$ is less than $\lambda_s 0$ and $\lambda_l 0$ is selectively positioned at a wavelength greater than about 700 nm; and

(b) a component which at least partially absorbs or reflects radiation in the wavelength region between $\lambda_s \theta$ and $\lambda_l 0$ at a normal angle of incidence (WGFC).

This optical body provides good reflectivity in the infrared region of the spectrum and improved shading coefficient at normal angles while still transmitting visible light at all desirable angles of incidence.

The WGFC functions to either absorb or reflect the infrared wavelengths that are not reflected by the film at normal angles because of the need to shift the reflective band of the film to higher wavelengths in order to minimize perceived colour changes at non-normal incidence. Depending on the placement of the WGFC relative to the film, it may not function at non-normal angles because the reflective band shifts to lower wavelengths, preferably coinciding with the wavelength region of the absorption or reflection of the WGFC. The WGFC may be incorporated into one or more of the film layers or incorporated into a separate or discrete part of the optical body, i.e. a separate layer from the film (a) that may be attached thereto by lamination. In this type, the WGFC (i.e. IRA) is incorporated into a separate layer adhered to the film (a). The WGFC may be a part of the film or separate from the film, depending on the characteristics of the film with which it is being combined.

The film (a) and the WGFC (b) may be combined so that the film is placed on a surface nearest the sun as practical because it is more efficient to reflect solar energy than to absorb it. Where possible, it is preferable that the sun's rays first encounter the film and then secondarily encounter the WGFC. In a multiple pane or two-ply windshield, the most preferable placement for the film is the exterior nearest the sun, the next preferable position is between the panes or plies. The film may be placed on the interior

surface but this allows absorption of solar light by the glass before the light reaches the film and absorption of part of the light reflected from the film. This arrangement may be preferable when considered from a UV protection standpoint, since it may be preferable to position the film away from the sun, allowing components that are less sensitive to UV to absorb this part of the light.

The WGFC (IRA) can be applied to either surface of the film (a), in a layer of glass or polymer, such as polycarbonate or acrylic, laminated to the film, or be present in at least one of the polymer layers of the film. From a solar energy standpoint, the WGFC is preferably on the innermost surface of the film (i.e. toward the interior and away from the sun) so that when the sun is at a high angle, the film reflective band shifts to lower wavelengths, essentially coinciding with the λ_{max} region of the dye. This is preferred because reflecting solar energy away from the film is preferred to absorbing it.

The amount of WGFC used in the optical body of the present invention may be varied depending on the specific nature of IRA and the end use application. Typically, when applied to the surface of the film, IRA is present on the surface at a concentration and coating thickness suitable to accomplish the desired infrared absorption and visible appearance. Typically, if the IRA is within an additional layer or within the multilayer optical body, the concentration ranges from about 0.05% to about 0.5% by weight, based on the total weight of the optical body. It is highly desirable that the IRA is finely divided to such an extent that the particle size is less than the wavelength of the incident light. If the IRA is non-polar solvent soluble and is heat stable, it can be coated or mixed in with solid plastic pellets and extruded.

However, the present IRA is not limited to use only in an optical body of this type, but may be used in any other optical body with a like purpose, i.e. attenuation of IR radiation.

(c) Detection/Handling Systems

Such systems conveniently comprise a detector to detect, and optionally to measure the strength of, an infra-red signal from an image on an article to be detected or a thermal signal (enhanced by the presence of an IRA in the image) and may feed this to an automated handling system for manipulation of the article in accordance with information in the signal or to a data handling system for stock recording or accounting.

The image may be formed by application of an ink to the article, especially a UV curable ink containing an IRA according to the present invention.

(i) UV Curable Ink

A suitable UV-curable ink comprises an alkoxyated or polyalkoxyated acrylate monomer, a photoinitiator and a colorant, such as that described in US 6,114,406 (the contents of which are incorporated herein by reference). A preferred UV-curable ink jet composition comprises, 80% to 95% by weight of a polyfunctional alkoxyated and/or

polyalkoxylated acrylate monomer material with respect to the total composition, a photoinitiator, an IRA and, optionally, a colorant.

The amounts of the acrylate monomer, photoinitiator, IRA and colorant may be varied according to the particular equipment and application. However, the amount of photoinitiator is preferably from 1% to 15% by weight of the total composition.

The polyfunctional alkoxyated or polyalkoxylated acrylate monomer material may comprise one or more di- or tri-acrylates or alkoxyated or polyalkoxylated acrylic monomers of higher functionality may be used alone or together with one or more di- and/or trifunctional materials. The number of alkyleneoxy groups is preferably from 1 to 20 per molecule of the monomer and each such group is preferably C₂₋₄-alkyleneoxy, more especially ethyleneoxy (EO) or propyleneoxy (PO).

Suitable polyfunctional alkoxyated or polyalkoxylated acrylates are alkoxyated, preferably ethoxyated or propoxyated, adducts of neopentylglycol diacrylates, butanediol diacrylates, trimethylpropane tri-acrylates and glyceryl triacrylate.

The ink may also contain up to 10%, by weight of a monofunctional alkoxyated or polyalkoxylated acrylate monomer, such as an alkoxyated, especially ethoxyated or propoxyated, adduct of one or more of tetrahydrofurfuryl acrylates, cyclohexyl acrylates, alkyl acrylates, nonyl-phenol acrylate and polyethylene- or polypropylene-glycol acrylates.

The ink may also contain up to 5%, by weight of a non-alkoxyated mono or polyfunctional radiation curable monomer, such as octyl acrylate, decyl acrylate, N-vinylpyrrolidone, ethyldiglycol acrylate, isobornyl acrylate, ethyl-hexyl acrylate, lauryl acrylate, butanediol monoacrylate, β -carboxyethyl acrylate, t-butyl acrylate, polypropyleneglycol monomethacrylate, 2-hydroxyethyl methacrylate, hexanediol di(meth)acrylate, tetraethyleneglycol diacrylate, tripropyleneglycol diacrylate, butanediol diacrylate, polyethyleneglycol diacrylates and triethyleneglycol dimethacrylate.

Examples of suitable commercially available photoinitiators are xanthenes, thioxanthenes, benzophenones, quinones and phosphine oxides. Examples of co-initiators that may be included with the primary photoinitiator include amines and aminobenzoates. Where the ink includes a primary and a co-initiator, the total amount is preferable within the aforementioned preferred range. Aminobenzoate and acrylated amine co-initiators are preferably used with the xanthone and/or thioxanthone primary photoinitiator.

By the term radiation curable is meant that the composition is curable by the application of UV radiation. Such a composition may be a substantially colourless curable varnish or base or may, if it contains a colorant (i.e. a material which provides visual colour or a related optical property, such as fluorescence), be an ink. Where a colorant is present, the ink preferably contains from 1% to 10% by weight of colorant with respect to the ink.

Suitable colorants fall into two classes, (a) dyes, which are substantially soluble in the ink composition and (b) pigments, which are dispersed in the ink composition in the

form of fine particles, usually with the aid of a suitable dispersant. Typical pigments include Pigment Red 57:1, Pigment Red 52:2, Pigment Red 48:2, Pigment Blue 15:3, Pigment Green 7, Pigment Yellow 83, Pigment Yellow 13 and Pigment White 6. If the colorant is or contains carbon black no added IRA is generally required because carbon black absorbs strongly in the IR region of the spectrum.

The ink may also contain other minor ingredients, such as, surfactants, levelling additives, photoinitiator stabilisers, wetting agents and pigment stabilisers. The latter may for example be of polyester, polyurethane or polyacrylate types, especially in the form of high molecular weight block co-polymers, and are typically incorporated at a level from 2.5% to 100% by weight of the pigment. Specific examples are Disperbyk 161 or 162 (BYK Chemie) and Solsperse hyperdispersants (Avedia). Suitable photoinitiator stabilisers include those disclosed in EP-A-0 465 039. Suitable surfactants are preferably non-ionic, such as Fluorad FC430 (ex 3M Corp.). Such surfactants (when present) are preferably included in an amount of 0.1% to 10% by weight of the total composition.

The ink or varnish is preferably substantially or totally free of organic solvent. Thus, it preferably contains less than 10%, more preferably less than 5%, especially less than 1% and more especially less than 0.1% of organic solvent by weight of the total composition.

The present IRA is not limited to use only in a UV curable ink this type, but may be used in any other UV curable ink in which it is soluble or dispersible.

(ii) Image Enhancement Systems

In such systems an IRA is added to a medium in order to enhance the strength of a thermal signal. One method for creating and detecting a thermal energy difference between a material and its surroundings comprises the steps of (i) adding an IRA according to the first aspect of the present invention to the material and/or to its surroundings, (ii) exposing the material and/or its surroundings to an input energy to create a thermal image; and (iii) measuring a change in the temperature of the material and/or its surroundings by means of a thermal image detector. The IRA is preferably added only to the material or only to the surroundings of the material in order to enhance the contrast between them.

The IRA may be used in solid form, in solution or in dispersion, or in vaporised or atomised to form an aerosol, and directed substantially to the target site or sites for imaging. Such direction may occur by a natural affinity of the IRA for the particular target site, or may be achieved by a targeted imaging process where a carrier is used, which may comprise vectors such as antibodies or other similar systems or the IRA may be directly placed in the target area. Alternatively direction may occur by restricting the mobility of the IRA so that it remains substantially in the target area, for example by controlling the inherent solubility, pH or lipid/water partition of the IRA.

The material may comprise any part of: a human or animal body, a plant or other vegetation, a building or engineering construction, a motor vehicle and applications in aviation transport or substrates such as paper, including rag paper, printer quality paper, currency grade paper, plastics-coated or laminated paper or other substrates typically used for documents or packaging.

The input energy is preferably a radiation source of preferably electronic energy of wavelength between 800 nm and 1000 nm. Typical irradiation sources include a simple halogen bulb, having an emission spectrum with a substantial portion in the near infra-red region, a Light Emitting Diode (LED) and a IR semiconductor laser, such the GaAlAs laser (emission at 785nm). Illumination times may be selected appropriately to give optimum imaging without significant direct heating which might interfere with the strength of the signal.

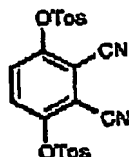
The thermal image detector may be any device able to detect and preferably record a thermal energy difference between or within a material and/or its surroundings, such as a thermal imaging camera (e.g. ThernaCAM® SC1000 camera, available from FLIR Systems, Boston, USA). The thermal imaging camera preferably comprises a charge couple device (CCD) sensitive to light of wavelength between 1.5 and 15 microns, more preferably between 3.4 and 5 microns. Image manipulation and data handling are achieved using appropriate computer software such as Thermagram® PRO95 software available from Thermoteknix Systems Limited, Cambridge, UK.

The IRA is conveniently added to the material and/or its surroundings in the form of a composition comprising the IRA and a liquid medium. The IRA may be dissolved or dispersed in the liquid medium. Suitable liquid media include water, a mixture of water and an organic solvent and an organic solvent free from water. It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or mixture of such solvents. Preferred water-miscible organic solvents include alcohols, more especially methanol, ethanol; dimethylsulfoxide; cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane-diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono-C₁₋₄-alkyl and C₁₋₄-alkyl-ethers of diols, more preferably mono-C₁₋₄-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

The present invention is further illustrated by the following Examples in which all parts and percentages are "by weight" unless otherwise indicated.

Example 1

Stage 1: 3,6-Bis(4-methylphenylsulfonyloxy)phthalonitrile



p-Toluenesulfonyl chloride (25.80g, 136mmol) was added to a suspension of 2,3-dicyanohydroquinone (10.00g, 62.5mmol) and potassium carbonate (34.50g, 250mmol) in acetone (75mL). The temperature of the flask rose rapidly, but stabilised after 2 minutes. The mixture was then heated to reflux and stirred for 2 hours, when TLC (eluting: CH₂Cl₂) indicated that all the starting 2,3-dicyanohydroquinone had been consumed. The mixture was allowed to cool to room temperature, poured into water (200ml), and stirred for 1 hour. Filtration gave the title compound as a colourless solid, which was washed with water (~30ml), pulled dry and dried in an oven (28.36g, 97%).

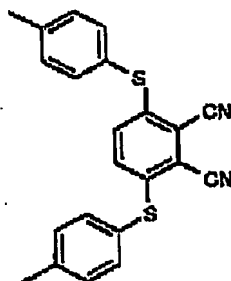
Analysis:

Gravimetric: Found: C, 55.8%; H, 3.3%; N, 6.0%; S, 13.5%;

C₂₂H₁₆O₆N₂S₂ requires; C, 56.4%; H, 3.4%; N, 6.0%; S, 13.7%;

Mass Spectral (EI⁺): 468 (M⁺, 80%); 155 (CH₃C₆H₄SO₂, 100%); 91 (CH₃C₆H₄, 90%).

Stage 2: 3,6-Bis(4-methylphenylthio)phthalonitrile



p-Thiocresol (3.41g, 27.5mmol) and potassium carbonate (3.80g, 27.5mmol) in DMF (40mL) were stirred at 110°C for 45 minutes, allowed to cool to ~60°C and 3,6-bis(4-methylphenylsulfonyloxy)phthalonitrile (ex Stage 1, 5.00g, 10.7mmol) added. The mixture was heated to 110°C for 4 hours when TLC (eluting: 30% ethyl acetate: isohexane) indicated that all the starting material from Stage 1 had been consumed. The mixture was then allowed to cool to room temperature, poured into water (100ml) and extracted with ethyl acetate (3x30ml). The combined organic extracts were dried over MgSO₄, filtered and concentrated to give a semisolid that was purified by flash column chromatography (gradient elution: 5%-10%-30% ethyl acetate:isohexane, finally dichloromethane) to give the title compound as a yellow solid (2.07g, 52%).

Analysis:

Gravimetric: Found: C: 69.9%; H: 4.4%; N: 7.3%; S: 16.9%;
(C₂₂H₁₈N₂S₂ requires: C: 70.9%; H: 4.3%; N: 7.5%; S: 17.2%)
Mass Spectral: (EI⁺): 372 (M⁺, 100%); 357 (M - CH₃, 5%); 123 (CH₃C₆H₄S, 15%);
91 (CH₃C₆H₄, 15%).

Stage 3: Octa-3,6-(4-methylphenylthio)-Li₂Pc

Lithium metal (removed from a piece immersed in paraffin oil) (0.14g, 20.0mmol) was added to a flask containing 3-methylbutanol (isopentanol) (50ml) and stirred until all the lithium metal had reacted. Then 3,6-bis(4-methylphenylthio)phthalonitrile (ex Stage 2, 15.0g, 40.3mmol) was added and the mixture heated to 120°C for 18 hours. Methanol (100ml) was then added and the mixture stirred for 1 hour. This was then filtered, the cake washed with a little more methanol and pulled dry to give the title compound as a green-brown solid (11.46g, 7.63mmol, 76%).

Stage 4: Octa-3,6-(4-methylphenylthio)-VOPc

Octa-3,6-(4-methylphenylthio)-Li₂Pc (ex Stage 3, 10.0g, 6.66mmol) and vanadium trichloride (2.10g, 13.4mmol) in quinoline (60ml) were heated to 200°C. After 8 hours the mixture was allowed to cool to room temperature. Dichloromethane (100ml) was added and the mixture filtered. The filtered solution was poured into water (100ml) and the organic layer separated. The aqueous layer was extracted with dichloromethane (3x30ml). Methanol was added (50ml) to the combined organic extracts and the dichloromethane removed via rotary evaporation. The mixture was then filtered, washed with more methanol and pulled dry to give the title compound as a dark brown/black solid (5.92g, 3.61mmol, 57%).

Analysis:

Mass Spectral: (FAB⁺) 1556 (MH⁺);

UV/VIS λ_{\max} = 851nm; ϵ_{molar} = 163,000.

Stage 5: Purification

Purification of the material from Stage 4, by flash column chromatography (1.40g (eluting: CH₂Cl₂), gave a dark brown/black solid (1.20g).

Analysis:

UV/VIS: λ_{\max} = 851nm; ϵ_{molar} = 179,534.

Example 2

Stage 1: Octa-3,6-chlorophthalocyanine

3,6-Dichlorophthalic anhydride (48.8g, 225mmol), urea (66.6g, 1110mmol) and ammonium molybdate (0.2g, 1.02mmol) in 1,2,4-trichlorobenzene (180ml) were heated to 155°C for 3 hours. Antimony (10.3g, 85mmol) and ammonium chloride (13.54g, 253mmol) were then added. The mixture was then heated to 200°C, stirred at this temperature for 6 hours and allowed to cool to room temperature. Ethanol (200ml) was then added and the mixture stirred at reflux for 1 hour and filtered on a Buchner funnel. The isolated solid was repeatedly added to refluxing ethanol (300ml) and refiltered (twice) and then

repeatedly added to conc. HCl (100ml) and filtered (twice). The isolated solid was finally added to ethanol (200ml), filtered and dried in an oven to give the product as a blue solid (18.2g, 23mmol, 41%).

Stage 2: Octa-3,6-(4-methylphenylthio)-H₂Pc

4-Methylphenylthiol (5.21g, 42mmol) and potassium hydroxide (2.35g, 42mmol) in quinoline (15ml) were heated to 120°C for 30 minutes. Octa-3,6-chlorophthalocyanine (from Stage 1, 3.30g, 4.2mmol) was then added and the mixture heated at 170°C for 1.6 hours after which it was allowed to cool to room temperature. Methanol (30ml) was added, the mixture was stirred for 30 minutes, then filtered and the solid washed with a little more methanol. The filtered solid was stirred with water (50ml), filtered and washed with methanol and pulled dry. Soxhlet extraction (CH₂Cl₂) gave, after concentration, the title compound as a brown solid (3.37g, 2.3mmol, 55%).

This process of this Stage 2 uses 10 molar equivalents of 4-methylphenylthiol per equivalent of octa-3,6-chlorophthalocyanine in order to ensure replacement of all the chlorine atoms by 4-methylphenylthio groups. Homologues of octa-3,6-(4-methylphenylthio)-H₂Pc containing from five to seven 4-methylphenylthio groups attached to the "3,6-carbon atoms" (the remaining "3,6-carbon atoms" carrying chlorine atoms) by the same process but using smaller amounts of 4-methylphenylthiol.

Stage 3: Octa-3,6-(4-methylphenylthio)-VOPc

Octa-3,6-(4-methylphenylthio)-H₂Pc is convertible to the lithium analogue octa-3,6-(4-methylphenylthio)-Li₂Pc using the method of V.M. Negrimovskii, M. Bouvet, E. A. Luk'yanets and J. Simon (see J.Porphyrins Phthalocyanines, 4, 248 [2000]) and thence into the title compound (vanadyloxy analogue) by the method set out in Example 1 Stage 4.

Example 3

Evaluation of Lightfastness

The lightfastness of the compound of Example 1, octa-3,6-(4-methylphenylthio)-VOPc (IRA 1), was compared to that of the closest known prior art compound, disclosed in the list on page 6 of EP 0155780, octa-3,6-(4-t-butylphenylthio)-VOPc (IRA PA).

Test images were prepared from 0.4% w/v dichloromethane solutions of each IRA by coating on to paper, with a Gravure printer, to give an OD of 0.6 for each image. Fading experiments were performed in an Atlas Ci5000 weatherometer (temp: 63°C, humidity: 40%). Absorbance spectra were measured before and after 24 hours exposure, using a Perkin-Elmer Lambda 19 UV/Vis/NIR spectrophotometer fitted with an Integrating sphere device, and the extent of fading for each compound (difference between original absorption and absorption after 24 hours exposure as a percentage of the original absorption) is set out in Table 1

Table 1

<u>Compound</u>	<u>Extent of Fading</u>
IRA 1	46%
IRA PA	67%

Example 4

Evaluation of Thermal Stability

The thermal stability of the compound of IRA 1 was compared to that of IRA PA (see Example 3).

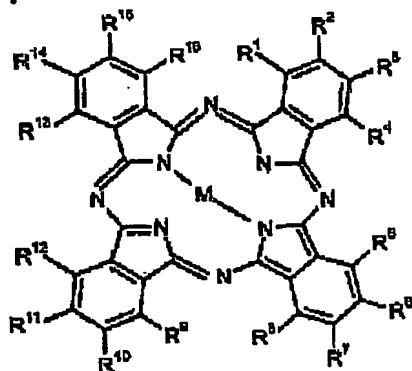
Thermogravimetric analysis was performed on a Perkin-Elmer TGA7 analyser by heating a sample of each compound from room temperature to 450°C at 10°C/minute and the trigger point, for the onset of thermal decomposition, of each compound is set out in Table 2.

Table 2

<u>Compound</u>	<u>Trigger Point</u>
IRA 1	340°C
IRA PA	300°C

CLAIMS

1. A phthalocyanine compound of Formula I



wherein at least 5 of the groups represented by R¹, R⁴, R⁶, R⁸, R⁹, R¹², R¹⁰ & R¹⁶ are independently -X-J or -X-L-X¹-, wherein

each J is independently selected from C₁₋₆-alkyl; C₂₋₆-alkenyl; C₄₋₈-cycloalkyl (each being optionally substituted by a group selected from C₁₋₄-alkoxy, C₁₋₄-alkylthio, C₆₋₁₂-aryl, C₆₋₁₂-arylthio, C₁₋₄-alkylsulphonyl, C₁₋₄-alkylsulphonylamino, C₁₋₄-alkylsulphoxide, amino, mono- and di-C₁₋₄-alkylamino, halogen, nitro, cyano and hydroxycarbonyl (-COOH), hydroxysulphonyl (-SO₃H) or dihydroxyphosphonyl (-PO₃H₂) or C₁₋₄-alkyl esters thereof) and from C₆₋₁₂-aryl (optionally substituted by a group selected from C₁₋₃-alkyl, C₁₋₃-alkoxy, C₁₋₃-alkylthio, C₁₋₃-alkylsulphonyl, C₁₋₃-alkylsulphonylamino, C₁₋₄-alkylsulphoxide, amino, mono- and di-C₁₋₃-alkylamino, halogen, nitro, cyano and hydroxycarbonyl, hydroxysulphonyl or dihydroxyphosphonyl, hydroxycarbonyl-C₁₋₃-alkyl, hydroxysulphonyl-C₁₋₃-alkyl, dihydroxyphosphonyl-C₁₋₃-alkyl or C₁₋₃-alkyl esters thereof);

each L is independently selected from C₁₋₆-alkylene and C₄₋₈-cycloalkylene (each being optionally substituted by a group selected from C₁₋₄-alkoxy, C₁₋₄-alkylthio, C₆₋₁₂-aryl, C₆₋₁₂-arylthio, C₁₋₄-alkylsulphonyl, C₁₋₄-alkylsulphonylamino, C₁₋₄-alkylsulphoxide, amino, mono- and di-C₁₋₄-alkylamino, halogen, nitro, cyano and hydroxycarbonyl, hydroxysulphonyl or dihydroxyphosphonyl or C₁₋₄-alkyl esters thereof); and from C₆₋₁₂-arylene (optionally substituted by a group selected from C₁₋₃-alkyl, C₁₋₃-alkoxy, C₁₋₃-alkylthio, C₁₋₃-alkylsulphonyl, C₁₋₃-alkylsulphonylamino, C₁₋₃-alkylsulphoxide, amino, mono- and di-C₁₋₃-alkylamino, halogen, nitro, cyano and hydroxycarbonyl, hydroxysulphonyl, dihydroxyphosphonyl, hydroxycarbonyl-C₁₋₃-alkyl, hydroxysulphonyl-C₁₋₃-alkyl or dihydroxyphosphonyl-C₁₋₃-alkyl or C₁₋₃-alkyl esters thereof);

M is an oxymetal group;

each X independently is S, Se, Te or NT;

each X^1 independently is S, Se, Te or NT and directly attached to a peripheral 3,6-carbon atom of another phthalocyanine compound of Formula I;
each T independently is H, alkyl or phenyl, or T & J, together with the N atom to which they are attached, form an aliphatic or aromatic ring provided this N atom is not positively charged; provided where J is aryl, T is not aryl;
and the remaining groups from R^1 to R^{16} are independently selected from H, halogen, -OJ, hydroxycarbonyl, hydroxysulphonyl, dihydroxyphosphonyl, hydroxycarbonyl-C₁₋₃-alkyl, hydroxysulphonyl-C₁₋₃-alkyl and dihydroxyphosphonyl-C₁₋₃-alkyl.

2. A phthalocyanine compound according to Claim 1 wherein each of R^1 , R^4 , R^6 , R^8 , R^9 , R^{12} , R^{13} & R^{16} is 4-methylphenylthio and each of R^2 , R^3 , R^5 , R^7 , R^{10} , R^{11} , R^{14} & R^{15} is H.

3. A phthalocyanine compound according to Claim 1 or Claim 2 wherein M is VO.

4. A method for the production of a lithographic printing plate containing a photosensitive layer comprising irradiating the photosensitive layer with an infra-red laser in accordance with pattern information wherein the photosensitive layer comprises an IRA according to any one of Claims 1 to 3.

5. A method of polymer welding in which a polymer material is irradiated with infra-red laser in a region where it is desired to form a weld wherein the polymer material comprises an IRA according to any one of Claims 1 to 3.

6. A method for the protection of an interior of a glazed structure against the heating effect of incident IR radiation by incorporating into the glazing or a layer forming part of the glazing an IRA according to any one of Claims 1 to 3.

7. A method for the attenuation of IR irradiation passing through a protective film by incorporating into the protective film or a layer forming part of the protective film an IRA according to any one of Claims 1 to 3.

8. A method for detecting an article carrying a superficial image by scanning with an infra-red detector wherein the image comprises an IRA according to any one of Claims 1 to 3.

9. A method for the formation of a permanent toner image on a substrate using an electrophotographic device incorporating an IR source to fix the temporary toner image on the substrate and/or provide an IR-readable permanent toner image wherein the toner comprises an IRA according to any one of Claims 1 to 3.

10. An article carrying an image adapted for machine reading in response to a reflective signal generated by scanning the image with infra-red radiation wherein the image comprises an IRA according to any one of Claims 1 to 3.

5

11. A method for the enhancement of a thermal signal comprising incorporating into the article from which the thermal signal is derived an IRA according to any one of Claims 1 to 3.

10

12. An ink comprising an IRA according to any one of Claims 1 to 3.

13. An ink according to Claim 12 also comprising a colorant

15

14. An ink according to Claim 12 or Claim 13 also comprising an alkoxyated or polyalkoxyated acrylate monomer and a photoinitiator.

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